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**DEVELOPMENT OF A NICKEL OXIDE/HYDROGEN MULTILAYER
BIPOLAR BATTERY FOR PULSED POWER - PHASE II**

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<p>This program is concerned with the development of a nickel oxide/hydrogen battery for pulsed power applications. It is based on thin film nickel oxide cathodes and metal hydride (e.g., LaNi₅) anodes. Thin film nickel oxides were prepared by reactive RF sputtering, chemical vapor deposition, anodic oxidation of nickel and by both cathodic and anodic precipitation of nickel hydroxide. Thin LaNi₅ films were prepared by rf sputtering from a target of the same composition.</p> <p>Initial nickel oxide pulse currents were several hundred mA/cm². Only a fraction of the electrode capacity was accessible at short times <10 msec. The LaNi₅ electrodes were electrochemically reversible for the H storage reaction, and pulse currents of thin film LaNi₅H_x electrodes were of the same magnitude as the nonsputtered NiO_x. Rates appear limited by surface reaction kinetics and by bulk diffusion in the anode and cathode, respectively. The best performance for NiO_x/hydride cells discharged in the pulsed mode through a load was ~350 mW/cm² as a 1 msec pulse. Difficulties were identified in scaling up the electrodes to practical thicknesses without sacrificing power density and mechanical adherence, and in achieving sufficient uniformity in capacity to implement multilayer bipolar stack battery configurations.</p>			
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1.0 OBJECTIVE

The Strategic Defense Initiative (SDI) will require on-board advanced power sources which can supply pulsed power into the megawatt range. Traditionally, pulsed power requirements have been met using devices which store energy in electric or magnetic fields and which ultimately derive their energy from the domestic power grid:

Energy \Rightarrow Source	Power \Rightarrow Source	Megawatt Pulses
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The weights of the energy and power sources are usually of little consequence for ground-based applications. In space or even in some terrestrial tactical applications (e.g., mobile rail gun), the weight required to produce the pulses is of critical importance.

There are clear advantages in weight of electrochemical systems for delivering multiple sequential power pulses. In order to achieve these advantages, batteries would have to be designed in which electrodes operated at 1-10 A/cm² (geometric) and in which the electrodes could be made quite thin and arranged into multilayer bipolar stacks [1]. We further specified the nickel oxide/hydrogen system as a likely rechargeable battery for development in this configuration. The nickel oxide cathode and hydride anode, it was proposed, can both be produced using vacuum and other thin film processing techniques which would be required for multilayer bipolar construction.

To place the issue of battery design into perspective, we present in Figure 1 the results of simple energy density and power density calculations for bipolar nickel oxide/hydride batteries [1]. For the purpose of the calculation, a baseline capacity for each electrode is assumed which is 52.4% of the theoretical value, the density factor for hexagonal close packed spheres, to take into account porosity. H₂LaNi₅ was used as the hydride, although other hydrides may be preferable. Each bipolar electrode was assumed to be supported on a 1 mil (24 μ m) thick Ti substrate, while a 0.5 mil separator saturated with KOH was assumed. The energy and power densities were then calculated for bipolar stacks as a function of electrode thickness for 0.1 to 10 A/cm² continuous discharge. Several conclusions can be drawn from these results:

1. Inert components dominate cell characteristics for active electrode thicknesses <1 μ m.
2. An optimal design point with respect to energy and power density exists for active electrode thicknesses between 10 and 50 μ m.
3. Our originally proposed goal of 10³ kW/kg will require that we achieve 5-10 A/cm² at about 1V in the pulsed mode.
4. The new high voltage batteries (100-200 V/cm of stack) would have discharge rates or 10³ to 10⁴C, which would be a revolutionary departure from current technology. For example, a cell comprised of 50 μ m thick nickel oxide electrodes would be discharged in 2.3 sec at 10 A/cm².

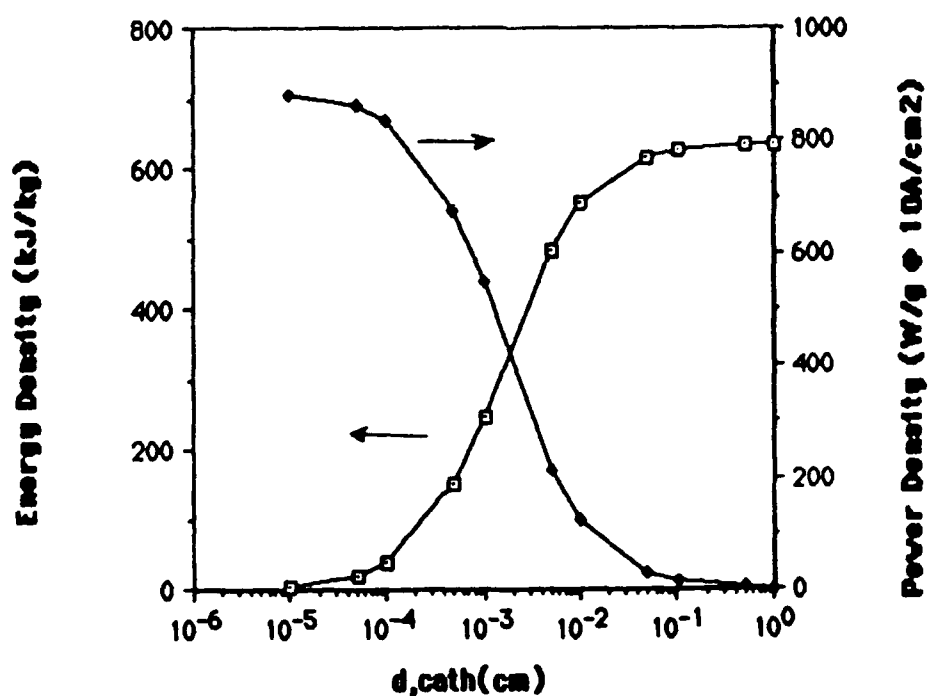
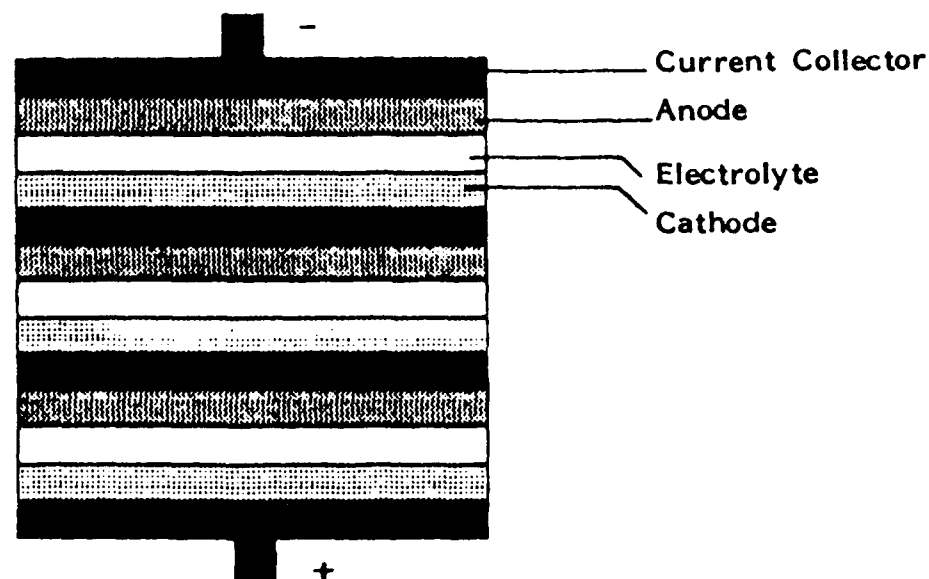


Figure 1. Schematic representation of a three-cell bipolar $\text{NiO}_x/\text{hydride}$ battery (not to scale) and calculated energy and power densities as a function of cathode thickness. A balanced anode capacity, 0.025 mm (1 mil) Ti substrate and 0.012 (0.5 mil) separator/electrolyte are assumed for the calculation.

2.0 ATTEMPTS TO AFFECT NiO_x MORPHOLOGY

A considerable portion of this program was devoted to the development of a high surface area substrate in order to improve the "macroporosity" on NiO_x electrodes. We demonstrated a direct correlation between electrode roughness determined by image analysis of scanning electron micrographs, and charge storage capacity [2]. We determined that in order to provide an advantage in a multilayer bipolar configuration over battery/capacitor combinations, that electrode thicknesses of 10-30 μm would be required. Higher thicknesses would lead to insufficient power densities, while lower thicknesses would overly compromise energy density. The experiments to produce planer NiO_x electrodes of this capacity are summarized in Table 1. The goal of etching substrate foils was to produce a high aspect ratio brush-type structure (e.g., 1 μm diameter posts separated by \sim 10 μm) into which the NiO_x could be deposited, e.g., by cathodic precipitation. Foils were both etched directly and with narrow line "Ronchi ruling" photoresist patterns (1:1 line:space ratio, 10 μm width). Although a high degree of surface roughness was observed, the morphology was difficult to control and predict. Photoresist patterns were undercut homogeneously in all cases except for pulse high current etching, in which it was reduced due to diffusion gradients within the grooves. These grooved substrates were employed in preparing some NiO_x electrodes. A number of experiments were carried out to prepare 10-30 μm thick planer porous Ni sinters on Ni substrates using conventional battery electrode preparation techniques (Table 1, Method D). These, however, failed to produce homogeneous sinters of thicknesses $<100\mu\text{m}$ (approximately).

Best results for adherent NiO_x deposits were obtained on Ni substrates patterned with 50 μ wide by 10 μm deep grooves using a photoresist mask and etching method B.⁴ (Table 1). NiO_x was cathodically precipitated from a solution of 2M Ni(NO₃)₂/0.3M NaNO₂, according to reaction (1):



The precipitated layer is then activated by anodization in 0.1M KOH. The reaction is inefficient since there is a competition between Ni⁺² and H⁺ for the electrogenerated OH⁻. In addition, the adhesion of the precipitated layer to the relatively smooth, planer substrates anticipated for the bipolar structure is a limiting factor. Capacity results for the bare substrate, a Ni substrate in which NiO_x was prepared by anodization of the bare metal, and the precipitated/anodized material are compared in Table 2. The maximum capacity that could be obtained was only approximately 0.7 C/cm², with higher deposition rates sometimes exhibiting slightly higher baseline capacities. Micrographs revealed a mushroom morphology with 2-5 μm features. Layers of >1 C/cm² were obtained by adding Co to the films (Table 3). It was determined that the maximum layer thickness could be obtained with a much shorter deposition time. Nevertheless, obtaining sufficiently thick NiO_x electrodes proved to be a major obstacle to realizing the proposed structures.

Table 1. Results of procedures for generating high surface area Ni substrates.

Method	Conditions	Result
A. Chemical Etching	<ol style="list-style-type: none"> 1) 20% HCl 2) Nitric Acid 3) Aqua Regia 4) GFS 5911 (17% Ce(IV), 4% HClO₄) 	Inhomogeneous morphology; process difficult to control/reproduce.
B. Electrochemical Etching	<ol style="list-style-type: none"> 1) 20% HCl; >50 cycles at 200 mV, 0.0 to -0.8V (SCE) 2) 20% HCl, 0.1V (SCE) constant potential 3) pH 1.5, sa. KCl, 0.2V (SCE) const. potential 4) 5M H₂SO₄, const. current pulses of 500 mA/cm², 5 msec on 1 msec open circuit 	All processes reveal foil grain structure; 0.5-10 μ m roughness features on grains. Method 4 best for etching high aspect ratio grooves defined by photoresist patterns.
C. Electrodeposition of Ni	Ni sulfamate plating bath, high current density	Porous Ni layers of ~50% density obtained; micromorphology not sufficiently porous.
D. Powder Sintering	<ol style="list-style-type: none"> 1) Ni(OH)₂ sat. filter paper 2) Ni(OH)₂/KOH paste 3) Ni(OH)₂/C black/KOH paste 4) Ni(OH)₂/graphite 5) Ni carbonyl methocel binder 	Method 5 is best, giving 10-15 μ m uniform, porous sinter.

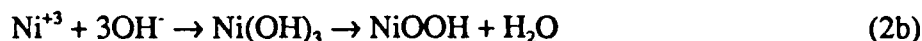
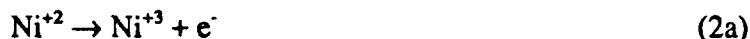
Table 2. Electrochemical properties of NiOx electrochemically precipitated onto high surface area Ni substrates. Anodic charge imbalance due to contribution from O₂ evolution.

Substrate				Electrode		
Etched		Anodized		Precipitated/Anodized		
CV Cap (mC/cm ²)	E _{max} (SCE)	CV Cap (mC/cm ²)	E _{max} (SCE)	Ni(OH) ₂ Dep (min x mA/cm ²)	CV Cap (mC/cm ²)	E _{max} (SCE)
5.26 (A)	1.43	42.0	1.43	8 x 77.5	673	1.46
4.14 (C)	1.36	41.0	1.27		481	1.27
14.4	1.41	61.1	1.40	12 x 51.7	592	1.46
3.76	1.35	49.0	1.29		499	1.25
11.7	1.43	32.9	1.40	24 x 25.8	592	1.46
3.8	1.37	23.9	1.33		461	1.29
7.95	1.43	37.9	1.42	32 x 19.4	452	1.47
3.9	1.33	32.6	1.31		403	1.27
8.19	1.41	41.7	1.42	8 x 77.5	76.5	1.41
3.74	1.35	35.1	1.29		66.2	1.29

Table 3. Electrochemical properties of Ni(Co)Ox electrochemically precipitated from 2M Ni(NO₃)₂/0.3M NaNO₂/10% Co(NO₃)₂.

Ni(OH) ₂ Dep (sec x mA/cm ²)	2 mV/sec		20 mV/sec	
	CV Cap (mC/cm ²)	E _{max} (SCE)	CV Cap (mC/cm ²)	E _{max} (SCE)
11.4 x 50	764 (A) 377 (C)	1.31 1.22	242 224	1.34 1.20
137 x 17	449 249	1.30 1.22	187 248	1.38 1.21
274 x 17	947 581	1.33 1.22	258 248	1.34 1.19
68.5 x 17	320 245	1.37 1.28	168 160	1.42 1.27
90 x 50	1730 890	1.27 1.19	338 313	1.32 1.15

Another study was conducted to investigate the electrochemical propagation and growth of NiOx, and the electrochemistry and kinetics of the deposits as a function of substrate, composition and quiescent aging. Deposition of the layers was compared using both reaction (1) and an anodic process (2):



Electrochemically, the different growth methods yielded similar films; however, reaction (2) could be used to grow films on carbon and other substrates with high hydrogen overpotentials. Films of up to 1 C/cm² were deposited onto vitreous carbon, for example, although they were generally nonadherent on the smooth substrate at this thickness. However, stirring was required to propagate films grown by reaction (3) due to the limitation by Ni⁺³ mass transfer. Reduction and oxidation of films ~ 0.1 μ thick produced a peak current function $iv^{-1/2}$ that is independent of sweep rate for $v = 5$ to 100 mV/s. Hence, the reaction is taking place throughout the film under conditions of semi-infinite linear diffusion.

A similar anodic reaction was used to grow films of CoOx, which were tentatively identified as Co₃O₄. The broad redox behavior of these films differed from NiOx in that the peak current was invariant as iv^{-1} , suggesting a surface-dominated reaction. This was interpreted as Co₃O₄ undergoing oxidation/reduction of the internal pore surfaces only. Thus, Co₃O₄ represents a conductive porous matrix into which the NiOx can be deposited. Mixed Ni/Co oxide electrodes were also prepared and had intermediate behavior between "redox" and "pseudocapacitive". These may be prototypes for high rate cathodes in pulse power batteries. A related electrode structure in which a conductive redox polymer was impregnated into a porous conductive oxide matrix was also investigated using electrochemical impedance spectroscopy to confirm this model [3].

3.0 PULSED OPERATION

The program dealt with experimental studies of both NiOx and hydride thin films as electrodes. Since no information on high rate, pulsed electrode processes in either material was available, all studies were carried out on very thin films of <100 mC/cm² capacity, corresponding to thicknesses of 0.1 to 0.2 μm.

NiOx films yielded pulsed discharge current densities ranging from <10 mA/cm² for some dense sputtered films to >500 mA/cm² for electrochemical and chemically precipitated materials. Since the films all had about the same baseline capacity (10-20 mC/cm² and ~ 0.1 μm thick), the current density variations must be ascribed to morphology [2]. Roughness factors of 1 to about 15 can be estimated for the lowest to highest current density films from double layer capacity measurements in a cathodic, nonelectrochemically active potential region. These values are lower limits, since the films become much more conductive in their oxidized forms. At the high end, a model of interconnected spherical voids would require an average void diameter of about 20 nm. However, scanning electron microscopic examination shows that roughness on a larger scale also correlates with the higher current densities.

Plots of capacity vs. $t^{1/2}$ demonstrate that the transient behavior is not controlled by a simple diffusion mechanism. Initial currents are smaller and later currents larger than expected. It is also clear that the extremely high capacitance is not readily accessible at very short time intervals. Limited electronic conductivity and electrode overvoltages (e.g., nucleation of a new phase) may contribute to this behavior. We have shown that the specific behavior of thin film electrodes depends strongly on the procedure of their fabrication which reflects a pronounced sensitivity towards small changes in composition (degree of hydration) structure and morphology. Hydrated nickel oxide films formed in solution showed the highest redox reaction rates followed by films prepared via thermal evaporation of nickel oxide and by reactive rf sputtering of nickel in water vapor and oxygen-containing environments. However, microscopic examination of the films indicated a correlation between macroscopic porosity, rate and charge acceptance. The sputtered films of nickel oxide prepared so far thus appear not to have the "xerogel" structure of, for example, sputtered iridium oxide [3]. The latter material, although appearing smooth and glassy under the SEM, nevertheless undergoes rapid oxidation and reduction throughout the film thickness. This appears to occur via molecular level voids, similar to those responsible for the high internal surface area of adsorbants like silica gel.

Current density will scale linearly with thickness for porous electrodes as long as resistive components remain low - i.e., 5 A/cm^2 might be achieved for a $1 \mu\text{m}$ thick film. Thus, development of thicker and highly conductive NiOx film electrodes is a primary concern. The limiting current densities are dependent on both diffusion of electrons and ions, and both vary inversely with thickness. Furthermore, the reduction in conductivity associated with the reduced electrode must be minimized in order to optimize pulsed discharge capacity (both Faradaic and non-Faradaic) and decrease polarization losses. This is likely to require some modification to the NiOx composition. Finally, to the extent that limiting thicknesses are found in these "microporous" NiOx films, it should be possible to realize additional gains in current density by enhancing macroporosity (i.e., $1\text{-}10 \mu\text{m}$ scale).

We also demonstrated preparation of thin film LaNi_3 electrodes by rf sputtering, which operated reversibly to electrochemical hydrogenation in 6N KOH . Maximum discharge rates of about 0.5 A/cm^2 were obtained for $0.1\text{-}0.2 \mu\text{m}$ films. The hydride electrode differs in operation from the nickel oxide. The electrical conductivities and H diffusion in the hydride bulk are both probably much higher than in amorphous nickel oxide. Rate limitation at this electrode appears to originate from the kinetics of H oxidation and possibly from the structure of the hydride/electrolyte interphase. Thus, the development of high rate thin film hydride electrodes will depend on catalyzing this reaction, on stabilizing the interphase, and on producing electrodes with high surface area.

The capabilities of thin film NiOx/hydride cells were defined and demonstrated using small cells with the best available electrodes from the program. The cell supplied trains of 100 1 msec power pulses into various loads. Initial power densities of 350 mW/cm^2 were obtained. After optimization for thickness, these electrodes may be capable of >100 sequential pulses of 10^{-3} sec duration, before recharge, each pulse with a power density of $5\text{-}10 \text{ W/cm}^2$. Such electrodes could be used to construct bipolar batteries with pulsed power densities of 10^5 W/kg .

4.0 CONCLUSIONS

The results of this program have indicated that the bipolar NiOx/hydride system, as we originally envisioned, continues to exhibit several fundamental obstacles for implementation. These obstacles include the following:

1. The NiOx electrodes studied exhibited slow oxidation reduction kinetics when loaded to practical capacities (e.g., $>0.1 \text{ C/cm}^2$). Thus, while peak pulsed discharge currents of up to 500 mA/cm^2 were observed on the 10 msec time scale for $\sim 0.01 \text{ C/cm}^2$ NiOx films, rate decreased with increasing thickness. This behavior is ascribed to the increase in electronic resistivity and decrease in ionic resistivity of the films with thickness. Furthermore, practical film thicknesses could not be obtained. Attempts to alleviate the reduction of capacity and mechanical properties with thickness by providing a highly porous, electrically conductive substrate were generally unsuccessful. However, initial results on incorporating electroactive NiOx into a conductive "pseudocapacitive" matrix (e.g., Co_3O_4 spinel) were promising.
2. NiOx layers had large variability in adherence, particularly under pulsed operation. Although this might be alleviated somewhat in a compressed stack, it affected the reproducibility of the electrode capacity. Reproducibility of individual capacity is key in bipolar stacks, since the stack capacity is determined by the lowest capacity cell unit.
3. Hydride electrodes were even slower than the NiOx electrodes, and were rate limiting in cell configurations. Attempts to enhance the rate with high surface area sintered hydride structures were unsuccessful.
4. Gas management in bipolar NiOx/hydride batteries will be a major problem, particularly if membrane separators with low gas diffusion rates are employed. The reason for this is that the NiOx electrode operates very close to the O_2 evolution potential. Thus, successful operation will depend on providing an H_2 (or H-hydride)/ O_2 recombination mechanism to compensate overcharge that is certain to occur within cell units of multi-bipolar stacks.

5.0 PUBLICATIONS

1. G.L. Holleck and R.D. Rauh, Development of a Nickel Oxide/Hydrogen Multilayer Bipolar Battery per Pulsed Power, Phase I Final Report, Contract No. N00014-86-C-0803, March 1987.
2. B. Aurian-Blajeni, A.G. Kimball, L.S. Robblee, G.L. Kahanda and M. Tomkiewicz, "Correlation between Charge Storage and Morphology", J. Electrochem. Soc. 134, 2637 (1987).

3. B. Aurian-Blajeni, S.C. Holleck and B.H. Jackman, "Organic/inorganic electrodes (ORINELS) with continuous phase components", J.Appl. Electrochemistry **19**, 331 (1989) (with NIH).

6.0 PRESENTATIONS

1. R. David Rauh, "High Rate Electrodes for Pulse Power", U.S. Army Workshop on Capacitors and Batteries for Pulse Power Applications, Ft. Monmouth, N.J., November 17-18, 1987.
2. R.D. Rauh, "Pulse Power Batteries", Meeting on Strategic Defense Initiative Technology: New Business Opportunities, New York, May 24-25, 1988.
3. R.D. Rauh, "High Rate Electrodes", ONR/DARPA/SDI Power Sources Meeting, Menlo Park, CA, March 29-30, 1989.

7.0 RESEARCH PERSONNEL

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